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LETTER TO THE EDITOR

Pretransition phenomena on the surface of ferroelastic crystal

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Abstract. The (001) surface of ferroelastic crystals $(NH_4)_4LiH_3(SO_4)_4$ (ALHS) and $Rb_4LiH_3(SO_4)_4$ (RLHS) has been studied using atomic force microscopy (AFM) at room temperature, i.e. 63 and 163 K above the phase transition, respectively. For ALHS the observations revealed the presence of a microstructure of 500×500 nm (in area) and 7–8 Å (in height), shaped as rectangles rotated by an angle of 33° with respect to the x-axis of the tetragonal system. As follows from the studies of elastic properties of this crystal by Brillouin spectroscopy, this angle is typical of the direction of the pure transverse mode corresponding to the soft elastic constant. As found from observations under a polarizing microscope, the ferroelastic domains of the W′ type appearing below T_C are rotated by a similar angle. The microstructure observed on the (001) surface of ALHS can be interpreted as a distinct pretransition phenomenon occurring far above the phase transition. In the case of RLHS, no modification of the (001) surface was detected.

On approaching the critical point various anomalies appear in the system's properties. One can ask which changes in which physical characteristics of the crystal, occurring far above T_C, indicates that the crystal in its prototype (high temperature) phase is approaching a phase transition. Let us restrict this question to the family of ferroic (ferroelectric and ferroelastic) materials and let us suppose that the transition is of the second order (to restrict the number of such physical quantities). If we are close enough to T_C we may observe temperature changes of the reverse susceptibility χ^{-1} (electrical in the case of ferroelectric and elastic, i.e. soft elastic constant in the case of ferroelastic) dropping with decreasing temperature and finally reaching zero at T_C. The above question was asked since there is no unambiguous definition of pretransition phenomena. Recently, the term embryonic fluctuations was introduced to account for the existence of incommensurate satellites of Bragg peaks in the paraelastic phase, located at the commensurate reciprocal points of the ferroelastic monoclinic phase of $Pb_3(PO_4)_2$ [1]. Similar results were reported for Ti–Ni [2] and Au–Cd alloys [3]. A phenomenological theory explaining the existence of such embryo or ghost lattice was developed by Fuchizaki and Yamada [4]. According to this model any crystal undergoing a first-order phase transition could show such anomalies if there is a strong coupling between the intrinsic order parameter and the strains.

Literature on the relationship between the bulk and surface-phase transitions gives a description of the phenomena, which could be classified as precritical. For instance, premelting of the Pb surface [5] and other metals and alloys [6] has been observed. Most recently, results of secondary-electron imaging (SEI) studies of the martensitic transformation in the single-crystal of cobalt have been reported [7]. Unlike in the case of Pb [5] or Cu_3Au [8] where the surface transformation was a kind of introduction to the upcoming bulk transition, the surface phase transition in cobalt was found to correspond to the late stage of martensitic [9] transformations. The theoretical work dealing with the problem has been done both for first- [10, 11] and second-order phase transitions [11].

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In this paper we present results of the atomic force microscopy (AFM) studies of the surface of two ferroleastic crystals ALHS and RLHS. We believe that in the case of ALHS we observed very distinct pretransition phenomena already at over 60 K above the phase transition temperature. Both crystals undergo the ferroelastic phase transition from the prototype tetragonal point group **4** to the monoclinic point group **2** at 232 and 132 K, respectively. Such a structural change is associated with the onset (at T_C) of the ferroelastic order parameter, i.e. spontaneous strain of the form $e_s = (e_{11} - e_{22}) + e_{12}$, where e_{11} and e_{22} are the tensor components of the strain along the x and y crystallographical directions of the monoclinic system, whereas e_{12} is proportional to the monoclinic angle. The Brillouin scattering studies of ALHS [12] and RLHS [13] revealed a distinct slow down of the pure transverse phonons. The related soft elastic constant c_{2S} was found to be very temperature dependent on both sides of the transition and in the case where ALHS reached zero at T_C. The pure-mode direction was calculated to 33° to the x-axis. This angle appears to be characteristic of the onset of ferroelasticity in ALHS. The ferroelastic domain structure of ALHS was observed with a polarizing microscope [14]. The domain pattern consisted of two types of mutually perpendicular walls rotated about the x-axis by approximately 33°. The observed domain walls are of the W′ type, which means that the equation describing their orientation contains all components of spontaneous strain [15]. The relationship between the wall orientation and the ferroelastic order parameter in this family of crystals has been reported in a recent paper [16]. The lattice parameters of the crystals studied in the ferroelastic state, including ALHS, were measured in our neutron scattering experiment [16] in a wide temperature range. From the results obtained it was possible to calculate the temperature dependence of the total spontaneous strain and its components and thus the orientation of domain walls. The orientation was found to make the angle of 33° with respect to the x-axis. It was also shown that in general W′ walls may change their orientation remaining perpendicular to each other only when the components of spontaneous strain appearing in the wall equation show different temperature behaviour.

The development of AFM enabled the investigation of the non-conducting materials' surfaces down to the atomic scale. A variety of applications has been considered including mechanical nanofabrication processes [17], nanotrybology [18] or recently introduced investigations of AFM application in the liquid environment [19]. Investigation of the surface of ferroleastic crystals is interesting because of the possible visualization of three-dimensional surface morphology due to the domain configuration. The relevant results can be found in [20–24]. Some authors [21] introduced a slight confusion calling the crystals, such as Rochelle Salt, $BaTiO_3$ or NdP_5O_{14} ferroelectric in connection with the AFM studies. We have to emphasize that the possibility of observing the distortion of their surfaces is strictly related to the ferroelasticity of the samples studied.

The AFM images of our samples were taken by a commercially available apparatus (OMICRON AFM). The instrument was working in contact mode under ambient conditions. The V-shaped silicon nitride cantilevers with integrated pyramidal tips characterized by a force constant of 6×10^{-2} N m^{-1} at an angle of 90° to their long axis and a loading ranging from 1–10 nN, were used. Crystals of ALHS and RLHS were grown isothermally at 310 K by the dynamical method from the acid aqueous solution of appropriate initial salts in stoichiometric proportion. The samples had the shape of plates (8 × 8 mm^2) oriented along the $x \equiv y$-axis of the tetragonal system. Since both materials showed a distinct cleavage plane perpendicular to the z-axis it was possible to prepare the samples of 1 mm thickness with the (001) plane to a very good quality. The plates prepared in this way were glued to the holder in the manner ensuring the direction of scans along the $y \equiv x$-axis. The observations were made at room temperature (295 K) i.e. 63 and 163 K above the ferroelastic phase transition of ALHS and RLHS, respectively, on samples which had not been cooled below T_C.

Figure 1 shows the AFM image of RLHS (001) taken of the samples cut out from another crystal. The 1100×1100 nm^2 picture shows a big flat area. The lower part of figure 1 shows the sample profile along the white arrow. The observed terrace is flat within $\pm$ 1 nm accuracy. A further increase of the resolution in the xy-plane did not reveal any modification of the sample surface.

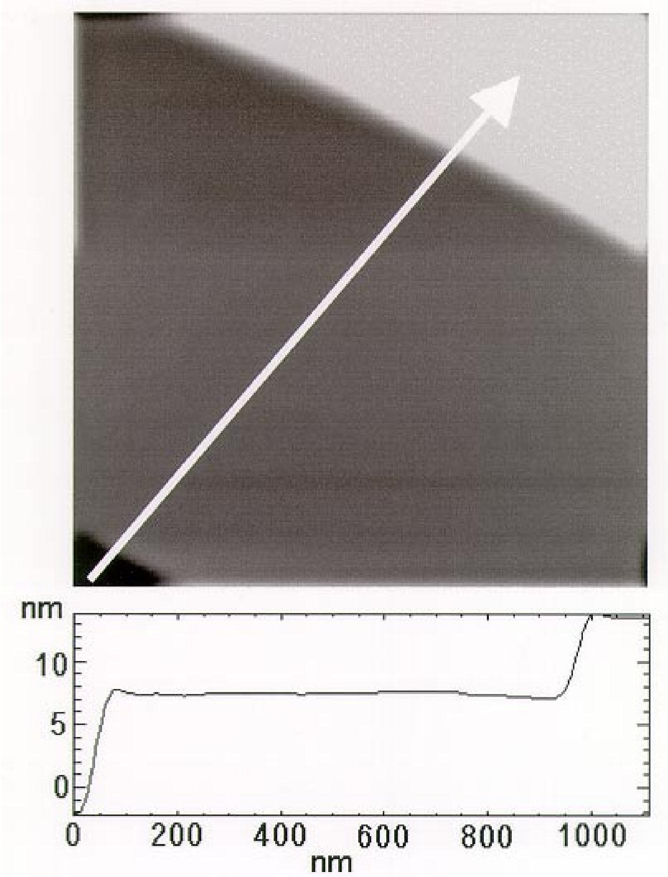

Figure 1. AFM image of RLHS; the (001) surface (upper part); height profile along the white arrow (bottom part.)

A different picture has been obtained for ALHS. In figure 2 we present the 2000×2000 nm^2 image of the (001) surface of the crystal. A modification can be clearly seen in the form of rectangular islands of average size of about 500×500 nm^2. The image analysis indicates that the islands are oriented in a constructed manner with respect to the fast scan direction. In figure 3 we present the AFM image of another sample of ALHS. When analysing this picture it appears that the microstructure observed on the (001) surface of ALHS shows a directional order. The islands are rotated at the same angle with respect to the $x \equiv y$-axis. Within the accuracy of $\pm 2^\circ$ we may conclude that this angle is 33° (or 57°) and indicates the future orientation of the domain walls in the ferroelastic phase of ALHS. The two perpendicular lines inserted in figure 3 indicate this orientation established both experimentally [14] and theoretically [16]. Figure 4 shows another (1500×1500 nm^2) image of the (001) surface. The big island of 1100×600 nm^2 is clearly seen. The inserted arrow indicates the direction of the height profile as presented at the bottom of figure 4. The height of the islands is very small (7–8 Å) when compared with their area and corresponds approximately to the quarter of the lattice constant (at 295 K $c = 29.50$ Å) [16].

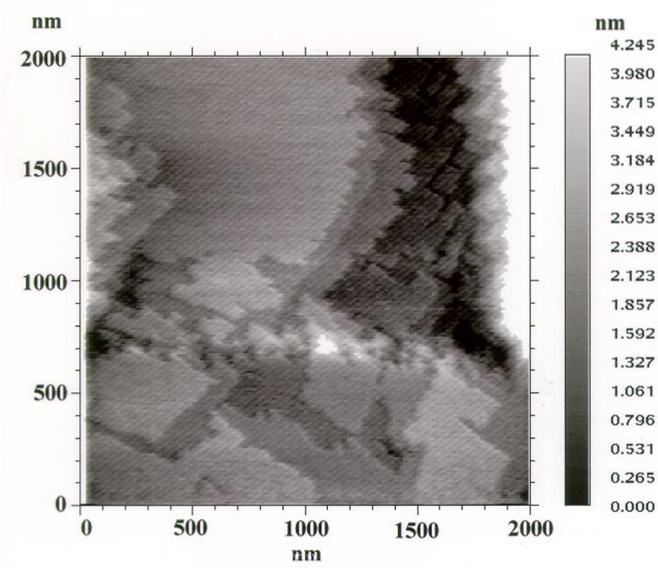

Figure 2. 2000×2000 nm^2 AFM image of ALHS crystal; the (001) surface.

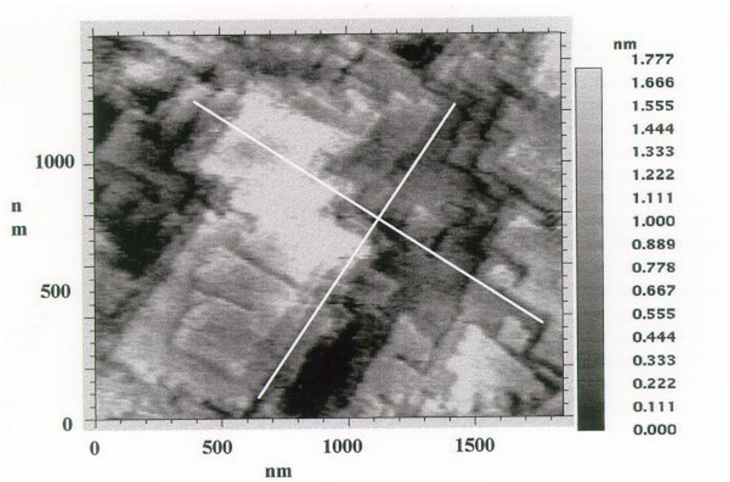

Figure 3. AFM image of ALHS (001) surface. Two perpendicular lines indicate the future orientations of ferroelastic domains.

Since our experiment was restricted to room temperature we can only speculate about the possible scenario of the surface of ALHS behaviour when the sample is approaching the phase transition temperature. The ferroelastic domain structure is an object a few orders of magnitude greater than the objects reported in this work. Figure 5 presents a typical profile of the elastic domain obtained on the basis of the images from [20–24] and the stack of islands

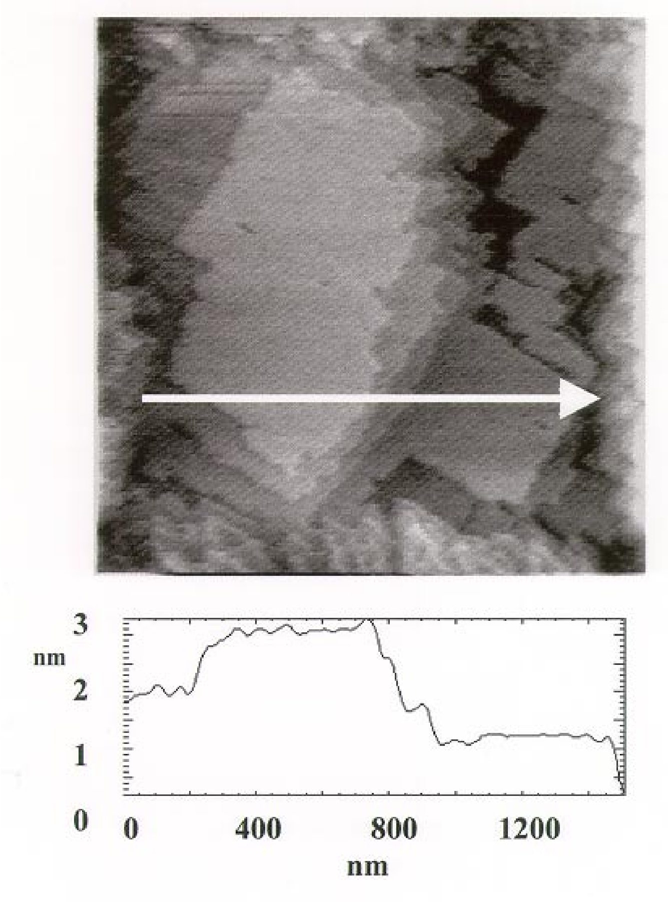

Figure 4. 1500×1500 nm^2 AFM image of ALHS (001) surface (upper part) and the height profile along the white arrow (bottom part).

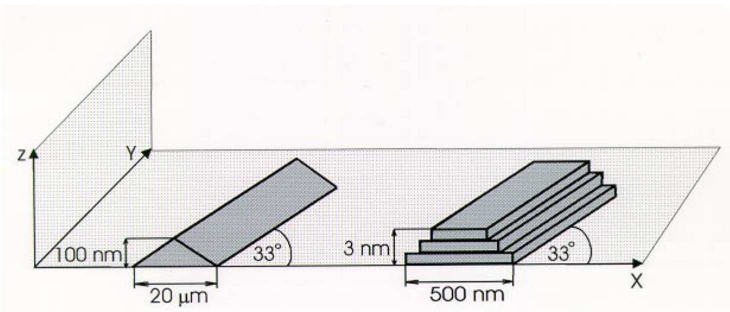

Figure 5. Schematic presentation of a typical profile of the ferroelastic domain and the stack of islands oriented in the same direction.

oriented at the same direction. The profile of the single domain is a triangle with a base of about 20 μm and a height of 100 μm. On such a background our islands are almost invisible, although their shape resembles that of the larger object. The ratio of the island width to its height is to an order of 10^2, so in some sense the domains and the islands are self-similar. We believe that in our crystal in the high-temperature phase there are certain distinguished directions of weaker bonds, unrelated to the tetragonal symmetry. Therefore, on cleaving the crystal a structure with the islands appears and makes traces of the future domain structure facilitating the elevation and indentation of the surface in the macro scale, below the phase transition temperature. It could be approximated by the effect of crushing a sheet of paper, which had been previously indented.

In conclusion, the first experimental observations of strong pretransition phenomena on the surface of a ferroelastic crystal have been reported. These phenomena involved an ordered reconstruction of the crystal surface observed a few ten degrees above T_C are strongly correlated with the future ferroelastic domain pattern.

Acknowledgements

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